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(54) PRODUCTION OF AGGREGATED DETERGENT COMPOSITION HAVING IMPROVED FLUIDITY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a production of aggregated detergent composition in which zeolite X is used to improve the fluidity of the final product.

SOLUTION: In the step (a), a granular detergent composition and a liquid binder are used to prepare a mixture (where the granular detergent composition contains a surfactant for detergent and the amount of the binder is about 1-6wt.% based on the granular detergent composition. In the step (b), the mixture prepared in the step (a) is mixed with zeolite X to prepare an objective mixture in which the amount of zeolite X is at least equal to that of the liquid binder in the composition prepared in the step (a).

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CLAIMS

[Claim(s)]

- [Claim 1] (a) Prepare the mixture of a granular detergent constituent and the liquid binder matter. (However, the amounts of said liquid binder of said granular detergent constituent are about 1 of said granular detergent constituent - 6 % of the weight of abbreviation, including a detergent surface active agent) (b) Process of the condensation detergent constituent characterized by what (however, the amount of Zeolite X is equal to the weight of the liquid binder in the constituent prepared at the process (a) at least) the constituent prepared at the process (a) and mixture with Zeolite X are prepared for.
- [Claim 2] The approach according to claim 1 the amounts of Zeolite X are about 1 of the weight of the liquid binder in the constituent prepared at the process (a) - a 2.5 times as many abbreviation as this.
- [Claim 3] The approach according to claim 2 a binder is an organic liquid.
- [Claim 4] The approach according to claim 2 a binder is alkoxy ** [which has an average of 3-16 alkoxy groups] C12 - C18 alcohol.
- [Claim 5] The approach according to claim 2 of blending with the mixture which prepared the hydrophobic sedimentation silica at the process (b) with the amount which is said about 0.1% - about 1% of mixture.
- [Claim 6] The approach according to claim 2 the granular detergent of a process (a) is the spray drying granular object from which the air by which the trap was carried out to miniaturization by giving before using it at a process (a) was removed.
- [Claim 7] An approach given in claim 1 thru/or any 1 term of 6 in which the granulation detergent constituent of a process (a) contains about 20% - about 95% of detergent surface active agents, and 5% - about 50% of detergency builder abbreviation.
- [Claim 8] The approach according to claim 7 a detergent surfactant is an anion composition surfactant.
- [Claim 9] The approach according to claim 8 chosen from the group which a detergency builder becomes from phosphate, poly phosphate, phosphonate, poly phosphonate, carbonate, borate, polyhydroxy sulfonate, polyacetate, carboxylate, and poly carboxylate.
- [Claim 10] (a) Prepare the mixture of a granular detergent constituent and the liquid binder matter. (However, the amounts of said liquid binder of said granular detergent constituent are about 1 of said granular detergent constituent - 6 % of the weight of abbreviation, including a detergent surface active agent) (b) Condensation detergent constituent characterized by being manufactured by the approach (however, the amount of Zeolite X being equal to the weight of the liquid binder in the constituent prepared at the process (a) at least) of preparing the mixture of the constituent and Zeolite X which were prepared at the process (a).
- [Claim 11] The product according to claim 10 whose amounts of Zeolite X are about 1 of the weight of the liquid binder in the constituent prepared at the process (a) - a 2.5 times as many abbreviation as this.
- [Claim 12] The product according to claim 11 blended with the mixture which prepared the hydrophobic sedimentation silica at the process (b) with the amount which is said about 0.1% - about 1% of mixture.
- [Claim 13] The product according to claim 11 whose binder is an organic liquid.
- [Claim 14] The product according to claim 11 whose binder is alkoxy ** [which has an average of 3-16 alkoxy groups] C12 - C18 alcohol.
- [Claim 15] A product given in claim 10 thru/or any 1 term of 13 in which the granulation detergent constituent of a process (a) contains about 20% - about 95% of detergent surface active agents, and 5% - about 50% of detergency builder abbreviation.
- [Claim 16] The product according to claim 15 whose detergent surfactant is an anion composition surfactant.
- [Claim 17] The product according to claim 16 chosen from the group which a detergency builder becomes from phosphate, poly phosphate, phosphonate, poly phosphonate, carbonate, borate, polyhydroxy sulfonate.

JP,09-302398,A [CLAIMS]

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polyacetate, carboxylate, and poly carboxylate.

[Translation done.]

1. A method for producing a polymeric material, comprising:
a) reacting a monomer having a carboxylic acid group with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
b) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
c) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
d) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
e) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
f) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
g) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
h) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
i) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
j) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
k) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
l) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
m) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
n) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
o) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
p) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
q) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
r) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
s) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
t) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
u) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
v) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
w) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
x) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
y) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;
z) reacting the polymeric material with a monomer having a carboxylic acid group, in the presence of a catalyst, to form a polymeric material;

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to manufacture of a free fluid condensation detergent granular object by the high density which uses the zeolite X as a liquid binder and a flow assistant.

[0002]

[Description of the Prior Art] Recently, in detergent industry, a big interest is held in manufacture of comparatively high bulk density, for example, the detergent granular object which has l. in 600g /or more.

[0003] Typically, the detergent granular object including an organic surface active agent and inorganic, or an organic builder is prepared by carrying out spray drying of the aqueous slurry of a component. Thus, typically, the obtained granular object has a consistency 300 [about] - 500g [/l.] abbreviation. In order to make the requirements for a high density detergent product agree, various approaches for giving such a product have been developed.

[0004] U.S. Pat. No. 5,133,924 specifications, such as Appel of issue, give the mixture of the granular component of a spray drying detergent constituent or a detergent constituent to two-step alligation on July 28, 1992, the porosity of a particle is decreased, and the approach of increasing a consistency by it is indicated. Liquids, such as water and a nonionic surface active agent, are added to a second stage story mixer by the case.

[0005] U.S. Pat. No. 5,164,108 specifications, such as Appel of issue, supply other detergent matter to a high speed mixer / precise machine on November 17, 1992 by the liquid acid precursor of an anionic surfactant, the water-soluble solid alkalinity builder, and the case, a liquid acid precursor is neutralized there, and the process of the high density detergent powder which consists of preparing powder, mixing powder in a medium-speed mixer subsequently, and decreasing the porosity of a powder particle by it is indicated. It is said that this patent may be produced about particle size distribution when the complicated problem processes a high activity (20% or more of namely, surfactants) constituent. It is indicated that these problems can be prevented by adding powdered matter, such as Zeolite A, to the second mixer.

[0006] JP,61-69897.A of April 10, 1986 public presentation is indicating the approach for manufacturing the dense condensation detergent product which consists of mixing with a binder (for example, nonionic surface active agent) and a "surface amelioration agent" (it being able to be aluminosilicate) from a spray drying detergent granular object including a surface active agent and a builder, after pulverizing a granular object by strong stirring in a blade mixer.

[0007] The U.S. Pat. No. 4,652,391 specification (bulk) of issue is indicating the spray drying detergent granular object whose surfactant is a nonionic surface active agent on March 24, 1987. This patent has pointed out that it should cool quickly, in order that a nonionic surface active agent may prevent that the granular object which comes from a spray tower is spread on the front face of a granular object. Such diffusion of a nonionic surface active agent decreases the fluidity of a granular product, and a consistency. When the warm weather bars quick cooling, it is said that "dusting" of the granular object can be carried out with a "plasticizer" (it is also called a "joint inhibitor"). Permutite (Zeolite A and Zeolite X) is indicated for this purpose.

[0008] Refer to 16th page - the 19th said U.S. Pat. No. 5,133,924 specification, the No. 5,164,108 specification, the No. 4,656,391 specification, JP,61-69897.A, and edition [of Perry's chemical en JINIAZU handbook / 6th] (1984) page.

[0009]

[Means for Solving the Problem] This invention prepares the uniform mixture of (a) granular detergent constituent and the liquid binder matter (the amounts of said liquid binder matter of said granular detergent

constituent are about 1 of said granular detergent constituent - 6 % of the weight of abbreviation, including a detergent surface active agent). (b) It is related with the process of the condensation detergent constituent characterized by what (the amount of Zeolite X is equal to the weight of the liquid binder in a process (a) at least, and are 1 - a 2.5 times as many abbreviation as this preferably) Zeolite X is contacted for in the constituent prepared at the process (a).

[0010] Moreover, this invention includes the constituent by said approach.

[0011] This invention relates to preparation (it is here, the granular detergent matter is mixed with the liquid binder matter of the amount of limitation, and the floc which has the particle size which increased by it as compared with the original detergent granular object arises) of a condensation detergent granular object. There is an inclination for the floc prepared by doing in this way by experience to be often adhesiveness, and it has become clear that it so has low free flowability. According to this invention, for the detergent floc which uses a liquid binder, when Zeolite X applied to said floc as a surface coating object, it was found out especially that it is an effective free flow assistant. In the case of most detergent applications, Zeolite A was more desirable than the ZEOO light X because of the effective and, general more good metal ion blockade force as a free flow assistant, but if there was a zeolite X in the case of the detergent floc using a liquid binder, now, it was found out that it is a still more effective free flow assistant than Zeolite A. In addition, it was found out by using Zeolite X as a free flow assistant by said floc that the product of high density is further obtained from what is obtained when using Zeolite A. Typically, the product manufactured by this method has bulk density higher 600g /than l.

[0012] The granular detergent constituent in the process (a) of the approach of granular detergent constituent this invention contains a detergent surfactant. The surfactant and other components of a granular constituent can be introduced into a process (a) as a separate component or preliminary preparation constituents, such as a spray drying detergent constituent, or mixture of one or more sorts of separate granular components, and a spray drying detergent constituent.

[0013] An anionic surfactant is a surfactant desirable although it is used here, and is well-known technically. It is as follows the example of representation of such a surfactant.

[0014] as a suitable anionic surfactant to use it here -- the inside of the molecular structure -- about 10- the water-soluble salt of the organic-sulfonic-acid resultant which has the alkyl group and sulfonate radical, or sulfate radical which has about 20 carbon atoms -- an alkali-metal salt, ammonium salt, and ARUKI roll ammonium salt are mentioned preferably ("alkyl" -- the alkyl part of an acyl group is included by the vocabulary). The example of the synthetic surfactant of this group Sodium alkylsulfate and an alkyl-sulfuric-acid potassium. By returning the glyceride of the first class in a premium grade (C8 - C18 carbon atom), secondary alcohol, for example, tallow, or palm oil especially or thing; and the alkyl group which are obtained by sulfurating what was generated by the oxo process -- a straight chain or branched chain arrangement -- about 9- the alkyl benzene sodium sulfonate which has about 15 carbon atoms, and an alkylbenzene-sulfonic-acid potassium -- for example It is the thing of a class given in a U.S. Pat. No. 2,220,099 specification and the No. 2,477,383 specification (it includes here as bibliography). the line whose number of averages of the carbon atom in an alkyl group is about 11-13 -- linear-alkyl-benzene sulfonate, has especially value.

[0015] Other suitable anionic surfactants to use it here The ether, palm-oil-fatty-acid monoglyceride sulfonic-acid sodium and the palm-oil-fatty-acid monoglyceride sodium sulfate of higher alcohol originating in alkyl glyceryl ether sulfonic-acid sodium especially tallow, and palm oil; fatty alcohol (for example) It has ethylene oxide of about one to 10 unit per molecule. An alkyl group A coconut or one mol of tallow alcohol, and 1-6 mols [of ethylene oxide] sodium salt or potassium salt of a sulfate of a resultant; about 8-12 carbon atoms It is the sodium salt or potassium salt of alkylphenol ethylene oxide ethereal sulfate which it has.

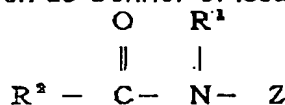
[0016] in addition, as a suitable anionic surfactant In a fatty-acid radical, about 6-20 carbon atoms It has. In an ester group about 1-10 carbon atoms water-soluble salt [of the ester of alpha-sulfonation fatty acid which it has]; -- the inside of an acyl group -- about 2-9 carbon atoms -- having -- and the inside of an alkane part -- 9- water-soluble salt [of a 2-acyloxy alkane-1-sulfonic acid]; which has about 23 carbon atoms -- about 12-20 carbon atoms beta-alkyloxy alkane sulfonate which has about 1-3 carbon atoms in water-soluble salt [of the olefin sulfonic acid which it has, and a paraffin sulfonic acid];, and an alkyl group, and has about 8-20 carbon atoms in an alkane part is mentioned.

[0017] A desirable anionic surfactant is the alkali-metal salt of C10 - 18 straight-chain alkylbenzene sulfonic acid, and C10 - 18 alkyl sulfuric acid. As for the desirable mode of this invention, an anionic surfactant consists of about 20% - about 40% of mixture of C10 of the weight ratio 2:1 [about] to 1:2 - 13 straight-chain alkyl benzene sodium sulfonate, and C12 - 16 sodium alkylsulfate.

[0018] The water-soluble salt of a higher fatty acid, i.e., "soap", is a useful anionic surfactant in this constituent, as this -- alkali-metal soap, for example, carbon number, about 8- about 24 -- the sodium salt, the potassium salt, ammonium salt, and ARUKI roll ammonium salt of a carbon number 12 [about] - about 18 higher fatty acid are mentioned preferably. Soap is generable with direct saponification of fats and oils, or neutralization of free fatty acid. The tallow soap and coconut soap of the sodium salt of the mixture of the fatty acid originating in palm oil and tallow and potassium salt, i.e., sodium, or a potassium are especially useful.

[0019] As a surfactant of other suitable classes to use it with the granular detergent constituent of a process (a), a nonionic surface active agent, a cationic surfactant, an amphoteric surface active agent, and a **** surfactant are mentioned.

[0020] As a typical nonionic surface active agent, the alkylene oxide condensate of the hydrocarbyl radical (for example, alkyl or alkylphenyl) on which a hydrocarbyl radical has the carbon atom of about 8 - 22 abbreviation is mentioned. A nonionic surface active agent also includes half-polar compounds, such as C8 - C22 amine oxide. The huge argument of a nonionic surface active agent is found out by U.S. Pat. No. 5,338,491 specifications, such as Connor of issue, on August 16, 1994. As a nonionic surface active agent,



it is a formula.

The inside of [type and R1 are H, C1 - C8. Hydrocarbyl, 2-hydroxyethyl, 2-hydroxypropyl or those mixture -- desirable -- C1 - C4 alkyl -- more -- desirable -- C1 Or C2 alkyl -- most -- desirable -- C1 Alkyl It is (namely, methyl) and is; R2, C5 - C32 hydrocarbyl part, desirable -- straight chain C7 - C19 alkyl or the alkenyl -- more -- desirable -- straight chain C9 - C17 alkyl or the alkenyl -- Most preferably Straight chain C11 - C19 alkyl or the alkenyl, or the line which has at least two pieces (in the case of a glyceraldehyde), or at least three hydroxyl (in the case of other reducing sugars) which are those mixture, and by which; Z was directly linked with the chain -- it has a hydrocarbyl chain -- a polyhydroxy hydrocarbyl part or it is the alkoxy ***** (preferably ethoxylation or propoxy-izing).] A ***** acid-amide surfactant is also mentioned. Z will be preferably guided from reducing sugar in the reduction amination reaction, and Z is a GURISHICHIRU part more preferably than. As suitable reducing sugar, a glyceraldehyde is mentioned to a glucose, a fructose, a maltose, a lactose, a galactose, a mannose and a xylose, and a list. It can use like each saccharide of the above [high glucose corn syrup, high fructose corn syrup, and high maltose corn syrup] as a raw material. The mix of the sugar component for Z can also be prepared with these corn syrup. He should understand that it is not what means eliminating other suitable raw materials. Preferably Z -CH2-(CHOH) n-CH2-OH, - CH(CH2-OH)-(CHOH)n-1-CH2-OH, - It will be chosen out of the group which consists of CH2-(CHOH)2-(CHOH (CHOR')) CH2-OH(s) (n is the integer of 1-5 among a formula, and R' is H, a ring type monosaccharide, or a polysaccharide), and those alkoxy ***** GURISHICHIRU whose n is 4, especially -CH2-(CHOH)4-CH2-OH are the most desirable.

[0021] The inside of said formula, and R1 For example, they can be methyl, ethyl, propyl, isopropyl, butyl, isobutyl, 2-hydroxyethyl, or 2-hydroxypropyl. For the highest foam formation, it is R1. They are methyl or hydroxyalkyl preferably. It will be R1 if low foamability is desired. They are C2 - C8 preferably. It is alkyl especially n-propyl, isopropyl, n-propyl, isopropyl, n-butyl, isobutyl, pentyl, hexyl, and 2-ethylhexyl.

[0022] As a specific example of this kind of amide surface active agent, C12-N-(3-MECHIKISHI propyl) glucamide and coconut n-methyl glucamide are mentioned. The further indication of this kind of amide surfactant can be found out on the U.S. Pat. No. 5,376,310 specifications of KURAIPU of issue on December 27, 1994.

[0023] As a cationic detergent surfactant, an ammonium surfactant R2 [for example,] among alkyl dimethyl ammonium halo GENAIDO and a formula [R2 y (OR3) [R4 y (OR3)] 2 R5 N+X- [type It is the alkyl or alkyl benzyl which has the carbon atom of about 8 - 18 abbreviation in an alkyl chain, every -- R3 -CH2 CH2- and -CH2 CH(CH3)- -- it chooses out of the group which consists of CH2 CH(CH2 OH)-, -CH2 CH2 CH2-, and those mixture -- having --; -- every -- R4 C1 - C4 alkyl -- C1 - C4 Hydroxyalkyl, benzyl, and two R4 The ring structure formed by combining a radical, - CH2 CHOHCHOHCOR6 CHOHCH2 OH (among a formula) R6 It is chosen out of the group which consists of the hexose polymer and hydrogen which have a hexose or about 1000 or less molecular weight (when y is not 0), and is; R5, R4 It is [whether it is the same and] an alkyl chain. R2+R5 the total number of a carbon atom -- about 18 or less -- it is --; -- each y -- 0- about 10 -- it is -- the sum of y value -- 0- it is about 15 and the surfactant which has] whose: X is a compatibility anion is mentioned.

[0024] Other useful cationic surfactants are indicated by the U.S. Pat. No. 4,228,044 specification of KYAMBURE of issue here on October 14, 1980. the second class whose aliphatic series radical of an amphoteric surface active agent can be a straight chain or a branched chain, the aliphatic series derivative of a tertiary amine, or a heterocycle type -- it can be widely indicated as the second class and the aliphatic series derivative of a tertiary amine. One of the aliphatic series substituents has the carbon atom of about 8 - 18 abbreviation on about eight carbon atoms and a type target at least, and at least one contains an anion aqueous-ized radical, for example, carboxy, sulfonate, and sulfate. It is related with the example of an amphoteric surface active agent, and they are the 19th **** of 18 lines of a U.S. Pat. No. 3,929,678 specification to Lauryn of December 30, 1975 issue etc. - the 35th line reference, a **** surfactant -- the second class and the derivative of a tertiary amine, and a heterocycle type -- it can be widely indicated as the derivative of the second class and the derivative of a tertiary amine or quaternary ammonium, quaternary phosphonium, or the third class sulfonium compound. It is related with the example of a **** surfactant and is 19th **** [to Lauryn of December 30, 1975 issue etc. / of a U.S. Pat. No. 3,929,678 specification / of 38 lines] - 22nd **** 48 line reference.

[0025] The still huger indication of various kinds of surfactants can be found out on the U.S. Pat. No. 3,664,961 specifications of Norris of issue on May 23, 1972.

[0026] Generally the surfactant will occupy about 30% - about 60% preferably 20% - about 95% of abbreviation of the granular detergent constituent of a process (a) prepared by this method.

[0027] Typically, probably, the detergent constituent prepared by this method contains the builder. Generally a useful builder is chosen from the phosphate of various kinds of water-soluble alkali metal, ammonium, or permutation ammonium, a polyphosphate, phosphonate, Pori phosphonate, a carbonate, a borate and a polyhydroxy sulfonate, Pori acetate, carboxylate, and a polycarboxylic acid salt by this invention. The alkali-metal salt of the aforementioned thing, especially sodium salt are desirable. Phosphate, carbonate, silicate, poly carboxylate, and those mixture are desirable although it is used here. Sodium tripolyphosphate, pyrophosphoric-acid 4 sodium, a sodium citrate, the tart rate mono-sodium succinate, tart rate disuccinic acid sodium, and those mixture are more desirable.

[0028] An inorganic phosphate builder's specific examples are the tripolyphosphate of sodium and a potassium, a pyrophosphate, the macromolecule metaphosphate that has polymerization degree about 6-21, and an orthophosphate. Other phosphorus builder compounds are indicated by a U.S. Pat. No. 3,159,581 specification, the No. 3,213,030 specification, the No. 3,422,137 specification, the No. 3,400,176 specification, and the No. 3,400,148 specification (those all are included here as bibliography).

[0029] A phosphorus-free inorganic builder's examples are zeolites, such as carbonate [of sodium and a potassium], bicarbonate, sesquicarbonate, and tetraborate 10 hydrate, and Zeolite A. As a useful water-soluble phosphorus-free organic builder, the Pori acetate of various kinds of alkali metal, ammonium, and permutation ammonium, carboxylate, a polycarboxylic acid salt, and a polyhydroxy sulfonate are mentioned here. The examples of polyacetate and a poly carboxylate builder are the sodium salt of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxy-disuccinic acid, mellitic acid, benzene polycarboxylic acid, and a citric acid, potassium salt, lithium salt, ammonium salt, and permutation ammonium salt.

[0030] The giant-molecule poly carboxylate builder is indicated by the U.S. Pat. No. 3,308,067 specification of the deal of issue on March 7, 1967. As such matter, the water-soluble salt of the homopolymer of aliphatic carboxylic acid, such as a maleic acid, an itaconic acid, mesaconic acid, a fumaric acid, aconitic acid, a citraconic acid, and a methylene malonic acid, and a copolymer is mentioned.

[0031] Other suitable poly carboxylate to use it here is polyacetal carboxylate given in the U.S. Pat. No. 4,144,226 specification of issue March 13, 1979 in the clutch field etc., and the U.S. Pat. No. 4,246,495 specification of issue March 27, 1979 in the clutch field etc.

[0032] Generally a builder occupies about 20% - about 40% preferably 5% - about 50% of abbreviation of the constituent prepared by this method. A builder can be added to floc, after being able to blend with the granular detergent constituent of a process (a) or mixing with Zeolite X.

[0033] Typically, bulking agent matter, such as a sodium sulfate and a sodium chloride, exists in the detergent constituent of a process (a) in the amount to about 40%.

[0034] The liquid of binder various kinds can be used as a binder for granular detergent components at the process (a) of the approach of this invention.

[0035] Water is a suitable binder. Similarly, the water solution with which even inorganic, an organic substance (Na₂O:SiO₂ ratio 2.0), for example, a sodium silicate, or about 65% even of polyacrylate polymers contain even about 35% more preferably [it is desirable and] to about 55% can be used. Generally, if the amount of solutes exceeds about 65%, aqueous dispersion liquid or a solution will become

viscosity too much, and it will result in it not being conveniently processible into uniform mixture with the granular detergent of the process (a) of this method. Moreover, the desirable approach of introducing a liquid binder into an approach is the approach of spraying on a granular detergent. A viscous solution is difficult to spray to altitude.

[0036] A non-ion organic liquid (melting point of about 7 degrees C or less) is desirable although it is used by the approach of this invention. The reason the desirable matter is a nonionic surface active agent is that they will contribute to the cleaning engine performance of a constituent. Refer to the argument of said nonionic surface active agent. These matter of the most ordinary class is alkoxy ***** organic compounds.

[0037] As suitable alkoxy ***** ion matter to use it as a binder of this invention, an average of 3-20 condensates of C12 which has 4-16 alkoxy parts preferably - 18 fatty alcohol are mentioned. An alcoholic radical may be methyl branching (oxo-radical) in saturation or mono-partial saturation, a line, or the 2nd place, and may be guided from natural or hydrogenation fat residue, and/or synthetic residue. The ethoxy rate guided from cetyl alcohol, stearyl alcohol, oleyl alcohol, and those mixture is especially suitable. the oleyl alcohol containing the tallow fatty alcohol with which an example contains an average of 4-8 ethylene oxide (EO) parts, the tallow fatty alcohol containing an average of 10-18 EO(s), and an average of 6-12 EO (s) — and they are those mixture again.

[0038] Other non-ion matter is 12 to alkoxy ** C24 (preferably C 14-18) alcohol (subsequently to the alcohol top concerned in the manufacture, 4-7 mols are added [1-3 mols of propylene oxide] preferably 4-20 mols of ethylene oxide). Eight to ethoxylation C12 alkylphenol containing 4-14 EO(s) is also suitable.

[0039] The non-ion organic liquid which is not a surface active agent can also be used as a binder of this invention. The examples of such matter are a polyethylene glycol and a polypropylene glycol.

[0040] A binder is most preferably used in about 3% - about 4.5% of amount about 2.5% to about 6% about 1% to about 6% to the whole quantity of a detergent component by the process (a) of this method.

[0041] In the process (b) of a zeolite X book method, the floc formed from an indispensable detergent component and an indispensable binder at the process (a) contacts the zeolite X of an amount equal to the amount of the liquid binder used at the process (a) of this method at least, and is mixed closely. Preferably, the amount of Zeolite X is 1 to 2.5 times the weight of the liquid binder used at the process (a).

[0042] Zeolite X is the synthetic aluminosilicate which can come to hand easily commercially from for example, the Union Carbide company and Philadelphia Quartz watch Company. A sodium salt form (zeolite 13X) has about 8A of apertures, and a calcium form (zeolite 10X) has about 7A of apertures. A sodium gestalt is desirable in order to use it here. Zeolite X should be a powder gestalt which has about 20 or less millimicrons of particle size. A desirable particle size is within the limits of about 5 - about 10 millimicrons.

[0043] Being attained when the further free fluid consistency of the constituent prepared by this method which improves and increased blends a hydrophobic sedimentation silica together with Zeolite X at the process (b) of this method was found out.

[0044] The suitable hydrophobic sedimentation silica to use it here is marketed, for example, is marketed as super nuts (Supernat) D10 and D17 from Degussa AG of German country Frankfurt / MAIN.

[0045] When using it at the process (b) of this method, the amount of a hydrophobic sedimentation silica is about 0.2% - about 0.4% preferably about 0.1% to about 1% to the weight of the mixture in a process (a).

[0046] By the matter case of arbitration, other useful matter can blend as a detergent component at the process (a) of this method with a detergent constituent. Or such matter can be added to floc, after mixing with Zeolite X or Zeolite X, and a sedimentation silica. As matter of arbitration, the surfactant, for example, the amphoteric surface active agent, the additional ***** surfactant, and additional cationic surfactant of a class are mentioned. The example of such a surfactant is indicated by the U.S. Pat. No. 3,664,961 specification of Norris of May 23, 1972 issue, and the U.S. Pat. No. 4,228,044 specification (it includes here as bibliography) of the camber of October 14, 1980 issue. As other arbitration components, a bleaching agent, a brightening agent, a bleaching activator, a foam increasing agent, foam suppressor, a cloudy inhibitor and corrosion inhibitor, a dirt suspending agent, a color migration inhibitor, a stain proofing agent, a color migration inhibitor, a germicide, pH regulator, a chelating agent, clay, and an enzyme are mentioned.

[0047] The granular constituent containing a processing surfactant is used at the process (a) of this method. This constituent can consist of a granular object from a spraying drying tower, or one or more sorts of particulate matters by which spray drying is not carried out. Or this constituent can be mixture with a spray drying granular object, other granular detergent components, for example, an additional surface active agent, and/or a builder, a bleaching agent, etc. Before mixing with a binder, eburnation of the granular constituent can be carried out. For example, after giving a granular constituent to mixing in high speed mixers, such as REDIGE (Loedige) CB, a SHUGI (Shugi) granulating machine, and DORAISU (Drais)

K-TTP, it can be given to mixing in medium-speed mixers, such as REDIGE KM and DORAISU K-T. For example, refer to a U.S. Pat. No. 5,133,924 specification and the No. 5,164,108 specification. Mixing with an eburnation detergent particle and a binder and the contact to said mixture and Zeolite X (or zeolite X plus sedimentation silica) are attained in a medium-speed mixer.

[0048] By making compactors, such as a BCS25 mold compactor from SHINTO Industrial Company, pass this granular constituent, the spray drying granular product which contains an additional desiccation granular detergent component in performing this method in order to manufacture free fluidity eburnation floc by the anionic surfactant and the case in a desirable approach is given to miniaturization, removes air, and forms a chip by it, for example. Subsequently, these chips can be ground and sifted out (for example, in the FITS mill), and a desired particle size can be obtained. Subsequently, an eburnation particle is mixed with a non-ion binder, and Zeolite X (or zeolite X plus sedimentation silica) is made to contact. Preferably, a liquid binder is added to a granular detergent constituent by spraying on a detergent (however, before adding Zeolite X) constituent at the time of mixing. Mixing with a granular detergent (make it those any to which eburnation of whether eburnation is carried out is not carried out), and a binder, and the contact to Zeolite X can be attained in a suitable mixer. The examples of a suitable mixer are a FUKAE (Fukae) ** type high speed mixer from FUKAE Industrial Company of Kobe, Hyogo in Japan, and a ribbon (Ribbon) mixer from Power REXX Company in Osaka Osaka in Japan.

[0049] Especially all the %s and ratios of a publication in this specification are weight criteria unless it refuses, all the documents stated by this detail letter are included as bibliography.

[0050] Although this invention is illustrated by the following example, the following example does not limit this invention.

[0051] Eburnation of the spray drying surfactant granular object which has the presentation of the example I following and the consistency of 290g/l. is carried out as follows.

Fatty alcohol sulfate 9.0% linear-alkyl-benzene sulfonate 30.0 sodium carbonates 21 sodium silicates 16 sodium sulfates Eight polyethylene glycols 0.3 brightening agents 0.4 moisture The usual component besides 4 The 11.3 total 100% [0052] A spray drying detergent granular object is continuously inserted in on the upper part of a roll mold compactor unit through the force feeder arranged in the upper part of a compactor roll, and a chip is manufactured. : whose pilot compactor unit operating condition is as follows - the rotational speed of a roll - 3.60rpm it is - the ammeter of a roll - 5.5A - it is - a roll pressure - 1.7-2.1t - it is - and the rotational speed of a force feeder - about 16.8.rpm it is - the ammeter of a force feeder is 3.0A. An miniaturization rate is about 56kg/hour as a chip. The chip consistency which comes out from a roll is 1.3-1.6g/cc. The amount of surfactants in a chip is still 39%.

[0053] A surface-active-agent chip is uniformly supplied to a pilot grinder (FITS mill). : whose pilot grinder operating condition is as follows - the rotational speed of a shaft - about 4726 rpm it is - the ammeters of a shaft are 6.0-7.2A, and use a blanking size 2.0mm screen. % on 850m of a grinding chip is 4.0 - 10.0%. Less than 150m % is 19 - 22%. having ground the bulk density of a grinding chip as - about 660 g/l it is . The amount of surfactants in this grinding granular object is still about 39%.

[0054] 9.85kg of eburnation grinding granular objects and the 1.58kg of the C16 second class sodium alkylsulfate (95% [of sodium alkylsulfate], 2% [of sodium sulfates], moisture / 3% of miscellaneous components) powder are inserted in a pilot REDIGE KM mixer (capacity of 50l.). A fill is temporary bulk density 700 g/l of a finished product. It follows and is 37%. It is 3000rpm about a chopper rate. It is 35rpm about a blade rate, maintaining. It sets up. A grinding surface-active-agent granular object and alkyl sulfate powder are mixed with for [sufficient] 70 seconds in a REDIGE mixer. Subsequently, poly pyrrolidone (color migration inhibitor) 30g is sprayed for 25 - 30 seconds into a REDIGE mixer. Subsequently, C14-C15EO9 heated by 70 degrees C 440g of alkyl ethoxy rate nonionic surface active agents is sprayed for 50 - 60 seconds on the matter in a REDIGE mixer. Subsequently, 13X810g [of zeolites] and hydrophobic sedimentation silica 50g and 100g of antifouling polymers are added / mixed for 200 seconds by the REDIGE mixer. Subsequently, 40g of perfume is sprayed for 30 - 40 seconds into a mixer. The amount of surfactants of the obtained product is about 45%. This product is sifted out by the 1180m screen. The sifted-out product has about 45% of sum total surface activity doses. This product is bulk density 781 g/l. It is the free fluidity granular object which it has:

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(54) 【発明の名称】 改良された流動特性を有する凝集化洗剤組成物の製造法

(57) 【要約】 (修正有)

【課題】ゼオライトXを最終製品の流動性改善のために使用した洗剤凝集体の製法を提供する。

【解決手段】(a) 粒状洗剤組成物と液体バインダー物質との混合物を調製し(ただし、前記粒状洗剤組成物は洗剤界面活性剤を含み且つ前記液体バインダーの量は前記粒状洗剤組成物の約1〜約6重量%である)、(b) 工程(a)で調製した組成物とゼオライトXとの混合物を調整する(ただし、ゼオライトXの量は工程(a)で調製した組成物中の液体バインダーの重量に少なくとも等しい)ことを特徴とする、凝集洗剤組成物の製法。

【特許請求の範囲】

【請求項1】(a)粒状洗剤組成物と液体バインダー物質との混合物を調製し(ただし、前記粒状洗剤組成物は洗剤界面活性剤を含み且つ前記液体バインダーの量は前記粒状洗剤組成物の約1～約6重量%である)、

(b)工程(a)で調製した組成物とゼオライトXとの混合物を調製する(ただし、ゼオライトXの量は工程(a)で調製した組成物中の液体バインダーの重量に少なくとも等しい)ことを特徴とする、凝集洗剤組成物の製法。

【請求項2】ゼオライトXの量が工程(a)で調製した組成物中の液体バインダーの重量の約1～約2.5倍である、請求項1に記載の方法。

【請求項3】バインダーが有機液体である、請求項2に記載の方法。

【請求項4】バインダーが平均3～16個のアルコキシ基を有するアルコキシ化 $C_{12}\sim C_{18}$ アルコールである、請求項2に記載の方法。

【請求項5】疎水性沈降シリカを前記混合物の約0.1%～約1%である量で工程(b)で調製した混合物に配合する、請求項2に記載の方法。

【請求項6】工程(a)の粒状洗剤が、工程(a)で使用する前にコンパクト化に付してトラップされた空気を除去した噴霧乾燥粒状物である、請求項2に記載の方法。

【請求項7】工程(a)の造粒洗剤組成物が洗剤界面活性剤約20%～約95%および洗浄性ビルダー約5%～約50%を含む、請求項1ないし6のいずれか1項に記載の方法。

【請求項8】洗剤界面活性剤が陰イオン合成界面活性剤である、請求項7に記載の方法。

【請求項9】洗浄性ビルダーがホスフェート、ポリホスフェート、ホスホネート、ポリホスホネート、カーボネート、ボレート、ポリヒドロキシスルホネート、ポリアセテート、カルボキシレート、およびポリカルボキシレートからなる群から選ばれる、請求項8に記載の方法。

【請求項10】(a)粒状洗剤組成物と液体バインダー物質との混合物を調製し(ただし、前記粒状洗剤組成物は洗剤界面活性剤を含み且つ前記液体バインダーの量は前記粒状洗剤組成物の約1～約6重量%である)、

(b)工程(a)で調製した組成物とゼオライトXとの混合物を調製する(ただし、ゼオライトXの量は工程(a)で調製した組成物中の液体バインダーの重量に少なくとも等しい)方法によって製造されたことを特徴とする、凝集洗剤組成物。

【請求項11】ゼオライトXの量が工程(a)で調製した組成物中の液体バインダーの重量の約1～約2.5倍である、請求項10に記載の製品。

【請求項12】疎水性沈降シリカを前記混合物の約0.1%～約1%である量で工程(b)で調製した混合物に

配合する、請求項11に記載の製品。

【請求項13】バインダーが有機液体である、請求項11に記載の製品。

【請求項14】バインダーが平均3～16個のアルコキシ基を有するアルコキシ化 $C_{12}\sim C_{18}$ アルコールである、請求項11に記載の製品。

【請求項15】工程(a)の造粒洗剤組成物が洗剤界面活性剤約20%～約95%および洗浄性ビルダー約5%～約50%を含む、請求項10ないし13のいずれか1項に記載の製品。

【請求項16】洗剤界面活性剤が陰イオン合成界面活性剤である、請求項15に記載の製品。

【請求項17】洗浄性ビルダーがホスフェート、ポリホスフェート、ホスホネート、ポリホスホネート、カーボネート、ボレート、ポリヒドロキシスルホネート、ポリアセテート、カルボキシレート、およびポリカルボキシレートからなる群から選ばれる、請求項16に記載の製品。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、液体結合剤および流動助剤としてのゼオライトXを使用しての高密度で自由流動性の凝集洗剤粒状物の製造に関する。

【0002】

【従来の技術および発明が解決しようとする課題】最近、洗剤産業において、比較的高い嵩密度、例えば、600g/リットル以上を有する洗剤粒状物の製造に大きな興味を持たれている。

【0003】典型的には、有機界面活性剤および無機または有機ビルダーを含む洗剤粒状物は、成分の水性スラリーを噴霧乾燥することによって調製されている。このようにして得られた粒状物は、典型的には、密度約300～約500g/リットルを有する。高密度洗剤製品の要件に合致させるために、このような製品を与えるための様々な方法が開発されてきた。

【0004】1992年7月28日発行のアベル等の米国特許第5,133,924号明細書は、噴霧乾燥洗剤組成物または洗剤組成物の粒状成分の混合物を2段階混合法に付して粒子の多孔度を減少させ、それによって密度を増大させる方法を開示している。水、非イオン界面活性剤などの液体が、場合によって、第二段階ミキサーに加えられる。

【0005】1992年11月17日発行のアベル等の米国特許第5,164,108号明細書は、陰イオン界面活性剤の液体酸前駆物質、固体の水溶性アルカリ性ビルダーおよび場合によって他の洗剤物質を高速ミキサー/緻密機に供給し、そこで液体酸前駆物質を中和し、それによって粉末を調製し、次いで、粉末を中速ミキサー中で混合して粉末粒子の多孔度を減少させることからなる高密度洗剤粉末の製法を開示している。この特許は、

複雑化した問題が高活性（即ち、界面活性剤20%以上）組成物を加工する場合に粒径分布に関して生ずることがあると述べている。これらの問題は、ゼオライトAなどの粉末状物質を第二ミキサーに加えることによって未然に防ぐことができることが開示されている。

【0006】1986年4月10日公開の特開昭61-69897号公報は、粒状物をブレードミキサー中で攪拌によって微粉碎した後、バインダー（例えば、非イオン界面活性剤）および「表面改良剤」（アルミノシリケートであることができる）と混合することからなる密な凝集洗剤製品を、界面活性剤およびビルダーを含む噴霧乾燥洗剤粒状物から製造するための方法を開示している。

【0007】1987年3月24日発行の米国特許第4,652,391号明細書（バルク）は、界面活性剤が非イオン界面活性剤である噴霧乾燥洗剤粒状物を開示している。この特許は、噴霧塔から来る粒状物が非イオン界面活性剤が粒状物の表面に拡散するのを防止するために迅速に冷却すべきであることを指摘している。非イオン界面活性剤のこのような拡散は、粒状製品の流動性および密度を減少させる。温暖な天候が迅速な冷却を妨げる場合は、粒状物は、「流動化剤」（「固結防止剤」とも称する）で「ダスティング」することができるとが述べられている。合成ゼオライト（ゼオライトAおよびゼオライトX）は、この目的で開示されている。

【0008】前記米国特許第5,133,924号明細書、第5,164,108号明細書、第4,656,391号明細書および特開昭61-69897号公報およびペリーのケミカル・エンジニアーズ・ハンドブック第6版（1984）第16頁～第19頁参照。

【0009】

【課題を解決するための手段】本発明は、（a）粒状洗剤組成物と液体バインダー物質との均一な混合物を調製し（前記粒状洗剤組成物は洗剤界面活性剤を含み且つ前記液体バインダー物質の量は前記粒状洗剤組成物の約1～約6重量%である）、（b）工程（a）で調製した組成物をゼオライトXと接触する（ゼオライトXの量は工程（a）中の液体バインダーの重量に少なくとも等しく、好ましくは1～約2.5倍である）ことを特徴とする凝集洗剤組成物の製法に関するものである。

【0010】また、本発明は、前記方法による組成物を包含するものである。

【0011】本発明は、凝集洗剤粒状物の調製（ここで、粒状洗剤物質を限定量の液体バインダー物質と混合し、それによって元の洗剤粒状物と比較して増大された粒径を有する凝集体が生ずる）に関する。経験によって、このようにして調製された凝集体がしばしば粘着性である傾向があり、それゆえ低い自由流動特性を有することが判明している。本発明によれば、液体バインダーを使用する洗剤凝集体のためには、ゼオライトXが、前

記凝集体に表面被覆物として適用した場合に特に有効な自由流動助剤であることが見出された。ゼオライトAも自由流動助剤として有効であり且つ一般により良い金属イオン封鎖力のため大抵の洗剤用途の場合にはゼオライトX以上に好ましいが、ゼオライトXは、液体バインダーを利用する洗剤凝集体の場合にあってはゼオライトAよりさらに有効な自由流動助剤であることが今も見出された。加えて、ゼオライトXを前記凝集体で自由流動助剤として使用することによって、ゼオライトAを使用する時に得られるものよりさらに高密度の製品が得られることが見出された。典型的には、本法によって製造された製品は、600g/リットルより高い嵩密度を有する。

【0012】粒状洗剤組成物

本発明の方法の工程（a）における粒状洗剤組成物は、洗剤界面活性剤を含む。粒状組成物の界面活性剤および他の成分は、工程（a）に別個の成分として、または噴霧乾燥洗剤組成物などの予備調製組成物として、または1種以上の別個の粒状成分と噴霧乾燥洗剤組成物との混合物として導入することができる。

【0013】陰イオン界面活性剤は、ここで使用するのに好ましい界面活性剤であり且つ技術上公知である。下記のものは、このような界面活性剤の代表例である。

【0014】ここで使用するのに好適な陰イオン界面活性剤としては、分子構造中に約10～約20個の炭素原子を有するアルキル基およびスルホン酸エステル基または硫酸エステル基を有する有機硫酸反応生成物の水溶性塩、好ましくはアルカリ金属塩、アンモニウム塩およびアルキロールアンモニウム塩が挙げられる（「アルキル」なる用語にはアシル基のアルキル部分が包含される）。この群の合成界面活性剤の例は、アルキル硫酸ナトリウムおよびアルキル硫酸カリウム、特に高級（C₈～C₁₈炭素原子）第一級または第二級アルコール、例えば、タローまたはヤシ油のグリセリドを還元することにより、またはオキソ法により生成されたものを硫酸化することによって得られるもの；およびアルキル基が直鎖または分枝鎖配置に約9～約15個の炭素原子を有するアルキルベンゼンスルホン酸ナトリウムおよびアルキルベンゼンスルホン酸カリウム、例えば、米国特許第2,220,099号明細書および第2,477,383号明細書（ここに参考文献として編入）に記載の種類のものである。アルキル基中の炭素原子の平均数が約11～13である線状直鎖アルキルベンゼンスルホネートが、特に価値がある。

【0015】ここで使用するのに好適な他の陰イオン界面活性剤は、アルキルグリセリルエーテルスルホン酸ナトリウム、特にタローおよびヤシ油に由来する高級アルコールのエーテル；ヤシ油脂肪酸モノグリセリドスルホン酸ナトリウムおよびヤシ油脂肪酸モノグリセリド硫酸ナトリウム；脂肪アルコール（例えば、ココナツまたは

タローアルコール) 1モルとエチレンオキシド1~6モルとの反応生成物の硫酸エステルナトリウム塩またはカリウム塩; 1分子当たり約1~10単位のエチレンオキシドを有し且つアルキル基が約8~12個の炭素原子を有するアルキルフェノールエチレンオキシドエーテル硫酸ナトリウム塩またはカリウム塩である。

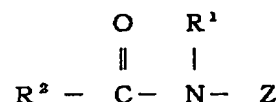
【0016】加えて、好適な陰イオン界面活性剤としては、脂肪酸基中に約6~20個の炭素原子を有し且つエステル基中に約1~10個の炭素原子を有する α -スルホン化脂肪酸のエステル水溶性塩; アシル基中に約2~9個の炭素原子を有し且つアルカン部分中に9~約23個の炭素原子を有する2-アシルオキシアルカン-1-スルホン酸の水溶性塩; 約12~20個の炭素原子を有するオレフィンスルホン酸およびパラフィンスルホン酸の水溶性塩; およびアルキル基中に約1~3個の炭素原子を有し且つアルカン部分中に約8~20個の炭素原子を有する β -アルキルオキシアルカンスルホネートが挙げられる。

【0017】好ましい陰イオン界面活性剤は、 $C_{10} \sim 18$ 直鎖アルキルベンゼンスルホン酸および $C_{10} \sim 18$ アルキル硫酸のアルカリ金属塩である。本発明の好ましい態様は、陰イオン界面活性剤が重量比約2:1から1:2の $C_{10} \sim 13$ 直鎖アルキルベンゼンスルホン酸ナトリウムと $C_{12} \sim 16$ アルキル硫酸ナトリウムとの混合物約20%~約40%からなるものである。

【0018】高級脂肪酸の水溶性塩、即ち、「石鹸」も、本組成物で有用な陰イオン界面活性剤である。これとしては、アルカリ金属石鹸、例えば、炭素数約8~約24、好ましくは炭素数約12~約18の高級脂肪酸のナトリウム塩、カリウム塩、アンモニウム塩およびアルキロールアンモニウム塩が挙げられる。石鹸は、油脂の直接ケン化により、または遊離脂肪酸の中和により生成できる。ヤシ油およびタローに由来する脂肪酸の混合物のナトリウム塩およびカリウム塩、即ち、ナトリウムまたはカリウムのタロー石鹸およびココナツ石鹸が、特に有用である。

【0019】工程(a)の粒状洗剤組成物で使用するのに好適な他の種類の界面活性剤としては、非イオン界面活性剤、陽イオン界面活性剤、両性界面活性剤および双性界面活性剤が挙げられる。

【0020】典型的な非イオン界面活性剤としては、ヒドロカルビル基が約8~約22個の炭素原子を有するヒドロカルビル基(例えば、アルキルまたはアルキルフェニル)のアルキレンオキシド縮合物が挙げられる。非イオン界面活性剤は、 $C_8 \sim C_{22}$ アミノオキシドなどの半極性化合物も包含する。非イオン界面活性剤の長大な議論は、1994年8月16日発行のコナー等の米国特許第5,338,491号明細書に見出される。非イオン界面活性剤としては、式

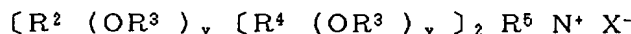


(式中、 R^1 はH、 $\text{C}_1 \sim \text{C}_8$ ヒドロカルビル、2-ヒドロキシエチル、2-ヒドロキシプロピル、またはそれらの混合物、好ましくは $\text{C}_1 \sim \text{C}_4$ アルキル、より好ましくは C_1 または C_2 アルキル、最も好ましくは C_1 アルキル(即ち、メチル)であり; R^2 は $\text{C}_5 \sim \text{C}_{32}$ ヒドロカルビル部分、好ましくは直鎖 $\text{C}_7 \sim \text{C}_{19}$ アルキルまたはアルケニル、より好ましくは直鎖 $\text{C}_9 \sim \text{C}_{17}$ アルキルまたはアルケニル、最も好ましくは直鎖 $\text{C}_{11} \sim \text{C}_{19}$ アルキルまたはアルケニル、またはそれらの混合物であり; Zは鎖に直結された少なくとも2個(グリセルアルデヒドの場合)または少なくとも3個のヒドロキシル(他の還元糖の場合)を有する線状ヒドロカルビル鎖を有するポリヒドロキシヒドロカルビル部分またはそのアルコキシ化誘導体(好ましくはエトキシ化またはプロポキシ化)である。)の脂肪酸アミド界面活性剤も挙げられる。Zは、好ましくは還元アミノ化反応において還元糖から誘導されるであろうし; より好ましくはZはグリシチル部分である。好適な還元糖としては、グルコース、フルクトース、マルトース、ラクトース、ガラクトース、マンノース、およびキシロース、並びにグリセルアルデヒドが挙げられる。原料として、高デキストロースコーンシロップ、高フルクトースコーンシロップ、および高マルトースコーンシロップが前記の個々の糖類と同様に利用できる。これらのコーンシロップによって、Z用糖成分のミックスを調製することもできる。他の好適な原料を排除することを意図するものでないことを理解すべきである。Zは、好ましくは $-\text{CH}_2 - (\text{CHOH})_n - \text{CH}_2 - \text{OH}$ 、 $-\text{CH}(\text{CH}_2 - \text{OH}) - (\text{CHOH})_{n-1} - \text{CH}_2 - \text{OH}$ 、 $-\text{CH}_2 - (\text{CHOH})_2 - (\text{CHOR}') - (\text{CHOH}) - \text{CH}_2 - \text{OH}$ (式中、 n は1~5の整数であり、 R' はHまたは環式単糖または多糖である)、およびそれらのアルコキシ化誘導体からなる群から選ばれるであろう。 n が4であるグリシチル、特に $-\text{CH}_2 - (\text{CHOH})_4 - \text{CH}_2 - \text{OH}$ が、最も好ましい。

【0021】前記式中、 R^1 は、例えば、メチル、エチル、プロピル、イソプロピル、ブチル、イソブチル、2-ヒドロキシエチル、または2-ヒドロキシプロピルであることができる。最高の起泡のためには、 R^1 は、好ましくはメチルまたはヒドロキシアルキルである。低起泡性が望まれるならば、 R^1 は、好ましくは、 $\text{C}_2 \sim \text{C}_8$ アルキル、特に n -プロピル、イソプロピル、 n -ブチル、イソブチル、 n -ペンチル、ヘキシルおよび2-エチルヘキシルである。

【0022】この種のアミド界面活性剤の特定例としては、 $\text{C}_{12} - \text{N} - (3\text{-メチキシプロピル})$ グルカミドおよびココナツ n -メチルグルカミドが挙げられる。この

種のアミド界面活性剤の更なる開示は、1994年12月27日発行のクライブの米国特許第5,376,310号明細書に見出すことができる。



〔式中、 R^2 は、アルキル鎖中に約8～約18個の炭素原子を有するアルキルまたはアルキルベンジル基であり、各 R^3 は $-CH_2CH_2-$ 、 $-CH_2CH(CH_3)-$ 、 $-CH_2CH(CH_2OH)-$ 、 $-CH_2CH_2CH_2-$ およびそれらの混合物からなる群から選ばれ、各 R^4 は $C_1 \sim C_4$ アルキル、 $C_1 \sim C_4$ ヒドロキシアルキル、ベンジル、2個の R^4 基を結合することによって形成された環構造、 $-CH_2CHOHCHOHCOR^6CHOHCH_2OH$ (式中、 R^6 はヘキソースまたは分子量約1000以下を有するヘキソース重合体) および水素 (y が0ではない時) からなる群から選ばれ、 R^5 は R^4 と同じであるかアルキル鎖であり、 $R^2 + R^5$ の炭素原子の合計数は約18以下であり、各 y は0～約10であり、 y 値の和は0～約15であり、 X は相容性陰イオンである〕を有する界面活性剤が挙げられる。

【0024】ここで有用な他の陽イオン界面活性剤も、1980年10月14日発行のキャンブレの米国特許第4,228,044号明細書に記載されている。両性界面活性剤は、脂肪族基が直鎖または分枝鎖であることができる第二級または第三級アミンの脂肪族誘導体、または複素環式第二級および第三級アミンの脂肪族誘導体と広く記載できる。脂肪族置換基の1つは、少なくとも約8個の炭素原子、典型的には約8～約18個の炭素原子を有し且つ少なくとも1つは陰イオン水溶化基、例えば、カルボキシ、スルホネート、サルフェートを含有する。両性界面活性剤の例に関しては、1975年12月30日発行のローリン等への米国特許第3,929,678号明細書第19欄第18行～第35行参照。双性界面活性剤は、第二級および第三級アミンの誘導体、複素環式第二級および第三級アミンの誘導体、または第四級アンモニウム、第四級ホスホニウムまたは第三級スルホニウム化合物の誘導体と広く記載できる。双性界面活性剤の例に関しては、1975年12月30日発行のローリン等への米国特許第3,929,678号明細書第19欄第38行～第22欄第48行参照。

【0025】各種の界面活性剤の更に長太な開示は、1972年5月23日発行のノリスの米国特許第3,664,961号明細書に見出すことができる。

【0026】界面活性剤は、一般に、本法によって調製された工程(a)の粒状洗剤組成物の約20%～約95%、好ましくは約30%～約60%を占めるであろう。

【0027】典型的には、本法によって調製された洗剤組成物は、ビルダーを含有するであろう。本発明で有用なビルダーは、一般に、各種の水溶性のアルカリ金属、アンモニウムまたは置換アンモニウムのリン酸塩、ポリ

【0023】陽イオン洗剤界面活性剤としては、アンモニウム界面活性剤、例えば、アルキルジメチルアンモニウムハロゲンナイド、および式

リン酸塩、ホスホン酸塩、ポリホスホン酸塩、炭酸塩、ホウ酸塩、およびポリヒドロキシスルホン酸塩、ポリ酢酸塩、カルボン酸塩、およびポリカルボン酸塩から選ばれる。前記のもののアルカリ金属塩、特にナトリウム塩が、好ましい。ホスフェート、カーボネート、シリケート、ポリカルボキシレート、およびそれらの混合物が、ここで使用するのに好ましい。トリポリリン酸ナトリウム、ピロリン酸四ナトリウム、クエン酸ナトリウム、タルトレートモノコハク酸ナトリウムおよびタルトレートジコハク酸ナトリウム、およびそれらの混合物が、より好ましい。

【0028】無機ホスフェートビルダーの特定例は、ナトリウムおよびカリウムのトリポリリン酸塩、ピロリン酸塩、重合度約6～21を有する高分子メタリン酸塩、およびオルトリン酸塩である。他のリンビルダー化合物は、米国特許第3,159,581号明細書、第3,213,030号明細書、第3,422,137号明細書、第3,400,176号明細書、および第3,400,148号明細書(それらのすべてをここに参考文献として編入)に開示されている。

【0029】無リン無機ビルダーの例は、ナトリウムおよびカリウムの炭酸塩、重炭酸塩、セスキ炭酸塩、四ホウ酸塩10水和物、およびゼオライトAなどのゼオライトである。ここで有用な水溶性無リン有機ビルダーとしては、各種のアルカリ金属、アンモニウムおよび置換アンモニウムのポリ酢酸塩、カルボン酸塩、ポリカルボン酸塩およびポリヒドロキシスルホン酸塩が挙げられる。ポリアセテートおよびポリカルボキシレートビルダーの例は、エチレンジアミン四酢酸、ニトリロ三酢酸、オキシジコハク酸、メリト酸、ベンゼンポリカルボン酸、およびクエン酸のナトリウム塩、カリウム塩、リチウム塩、アンモニウム塩および置換アンモニウム塩である。

【0030】高分子ポリカルボキシレートビルダーは、1967年3月7日発行のディールの米国特許第3,308,067号明細書に記載されている。このような物質としては、マレイン酸、イタコン酸、メサコン酸、フマル酸、アコニット酸、シトラコン酸、メチレンマロン酸などの脂肪族カルボン酸の単独重合体および共重合体の水溶性塩が挙げられる。

【0031】ここで使用するのに好適な他のポリカルボキシレートは、1979年3月13日にクラッチフィールド等に発行の米国特許第4,144,226号明細書および1979年3月27日にクラッチフィールド等に発行の米国特許第4,246,495号明細書に記載のポリアセタールカルボキシレートである。

【0032】ビルダーは、一般に、本法によって調製さ

れる組成物の約5%～約50%、好ましくは約20%～約40%を占める。ビルダーは、工程(a)の粒状洗剤組成物に配合でき、またはゼオライトXと混合した後に凝集体に添加できる。

【0033】硫酸ナトリウム、塩化ナトリウムなどの充填剤物質は、典型的には、工程(a)の洗剤組成物に約40%までの量で存在する。

【0034】バインダー

各種の液体は、本発明の方法の工程(a)で粒状洗剤成分用バインダーとして使用できる。

【0035】水が、好適なバインダーである。同様に、無機または有機物質、例えば、ケイ酸ナトリウム($\text{Na}_2\text{O}:\text{SiO}_2$ 比2.0)またはポリアクリレート重合体約65%まで、好ましくは約55%まで、より好ましくは約35%までを含有する水溶液は、使用できる。一般に、溶質量が約65%を超えると、水性分散液または溶液が粘稠になりすぎ、本法の工程(a)の粒状洗剤との均一な混合物に好都合に加工することができない結果となる。また、液体バインダーを方法に導入する好ましい方法は、粒状洗剤上に噴霧する方法である。高度に粘稠な溶液は、噴霧することが困難である。

【0036】非イオン有機液体(融点約7℃以下)は、本発明の方法で使用するのに好ましい。好ましい物質は、非イオン界面活性剤である、その理由は、それらが組成物のクリーニング性能に寄与するであろうからである。前記非イオン界面活性剤の議論参照。最も普通の種類のこれらの物質は、アルコキシ化長鎖有機化合物である。

【0037】本発明のバインダーとして使用するのに好適なアルコキシ化非イオン物質としては、平均3～20個、好ましくは4～16個のアルコキシ部分を有する $\text{C}_{12\sim 18}$ 脂肪アルコールの縮合物が挙げられる。アルコール基は、飽和またはモノ不飽和、線状または2位でメチル分枝(オキシ基)であってもよく且つ天然産または水素添加脂肪残基および/または合成残基から誘導されてもよい。セチルアルコール、ステアシルアルコールおよびオレイルアルコールおよびそれらの混合物から誘導されるエトキシレートが、特に好適である。例は、平均4～8個のエチレンオキシド(EO)部分を含有するタロー脂肪アルコール、平均10～18個のEOを含有するタロー脂肪アルコールおよび平均6～12個のEOを含有するオレイルアルコール、そしてまたそれらの混合物である。

【0038】他の非イオン物質は、アルコキシ化 $\text{C}_{12\sim 24}$ (好ましくは $\text{C}_{14\sim 18}$)アルコール(その製造においてプロピレンオキシド1～3モル、次いで、エチレンオキシド4～20モル、好ましくは4～7モルを当該アルコール上に付加する)である。4～14個のEOを含有するエトキシ化 $\text{C}_8\sim 12$ アルキルフェノールも、好適である。

【0039】界面活性剤ではない非イオン有機液体も、本発明のバインダーとして使用できる。このような物質の例は、ポリエチレングリコールおよびポリプロピレングリコールである。

【0040】バインダーは、本法の工程(a)で洗剤成分の全量に対して約1%～約6%、好ましくは約2.5%～約6%、最も好ましくは約3%～約4.5%の量で使用される。

【0041】ゼオライトX

本法の工程(b)において、工程(a)で必須の洗剤成分およびバインダーから形成された凝集粒子は、本法の工程(a)で使用した液体バインダーの量に少なくとも等しい量のゼオライトXと接触し且つ緊密に混合される。好ましくは、ゼオライトXの量は、工程(a)で使用した液体バインダーの重量の1～2.5倍である。

【0042】ゼオライトXは、例えば、ユニオン・カーバイド・カンパニーおよびフィラデルフィア・クォーツ・カンパニーから商業的に容易に入手できる合成アルミノシリケートである。ナトリウム塩形(ゼオライト13X)は孔径約8オングストロームを有し且つカルシウム形(ゼオライト10X)は孔径約7オングストロームを有する。ここで使用するためには、ナトリウム形態が好ましい。ゼオライトXは、粒径約20ミリミクロン以下を有する粉末形態であるべきである。好ましい粒径は、約5～約10ミリミクロンの範囲内である。

【0043】本法によって調製された組成物の自由流動性の更なる改善および増大された密度は、疎水性沈降シリカを本法の工程(b)でゼオライトXと一緒に配合した場合に達成されることが見出された。

【0044】ここで使用するのに好適な疎水性沈降シリカは、市販されており、例えば、独国フランクフルト/マインのデグッサAGからスーパーナット(Supernat)D10およびD17として市販されている。

【0045】本法の工程(b)で使用する時には、疎水性沈降シリカの量は、工程(a)中の混合物の重量に対して約0.1%～約1%、好ましくは約0.2%～約0.4%である。

【0046】任意の物質

場合によって、洗剤組成物で有用な他の物質が、本法の工程(a)で洗剤成分として配合できる。或いは、このような物質は、ゼオライトX、またはゼオライトXおよび沈降シリカと混合した後に凝集体に添加することができる。任意の物質としては、追加の種類の界面活性剤、例えば、両性界面活性剤、双性界面活性剤および陽イオン界面活性剤が挙げられる。このような界面活性剤の例は、1972年5月23日発行のノリスの米国特許第3,664,961号明細書および1980年10月14日発行のキャンバーの米国特許第4,228,044号明細書(ここに参考文献として編入)に開示されている。他の任意成分としては、漂白剤、増白剤、漂白活性

剤、増泡剤、抑泡剤、曇り防止剤および腐食防止剤、汚れ沈殿防止剤、染料移動抑制剤、防汚剤、染料移動抑制剤、殺菌剤、pH調整剤、キレート化剤、粘土および酵素が挙げられる。

【0047】加工

界面活性剤を含む粒状組成物は、本法の工程(a)で使用する。この組成物は、噴霧乾燥塔からの粒状物または噴霧乾燥されていない1種以上の粒状物質からなることができる。あるいは、この組成物は、噴霧乾燥粒状物と他の粒状洗剤成分、例えば、追加の界面活性剤および／またはビルダー、漂白剤などとの混合物であることができる。バインダーと混合する前に、粒状組成物を緻密化することができる。例えば、粒状組成物を、レディゲ(Loedige)CB、シューギ(Shugi)造粒機、ドライス(Drais)K-TTPなどの高速ミキサー中での混合に付した後、レディゲKM、ドライスK-Tなどの中速ミキサー中での混合に付すことができる。例えば、米国特許第5,133,924号明細書および第5,164,108号明細書参照。緻密化洗剤粒子とバインダーとの混合および前記混合物とゼオライトX(またはゼオライトXプラス沈降シリカ)との接触は、中速ミキサー中で達成される。

【0048】自由流動性緻密化凝集体を製造するために本法を行うのに好ましい方法においては、陰イオン界面活性剤および場合によって追加の乾燥粒状洗剤成分を含む噴霧乾燥粒状製品は、例えば、この粒状組成物をシント・インダストリアル・カンパニーからのBCS25型コンパクターなどのコンパクターに通過させることによってコンパクト化に付して空気を除去し、それによってチップを形成する。次いで、これらのチップを粉碎し(例えば、フィッツ・ミル中で)、篩分けして所望の粒径を得ることができる。次いで、緻密化粒子を非イオンバインダーと混合し、ゼオライトX(またはゼオライトXプラス沈降シリカ)と接触させる。好ましくは、液体バインダーを、混合時に(しかし、ゼオライトXを加える前)洗剤組成物上に噴霧することによって粒状洗剤組成物に加える。粒状洗剤(緻密化されているか緻密化されていないかのいずれにせよ)とバインダーとの混合、およびゼオライトXとの接触は、好適なミキサー中で達成することができる。好適なミキサーの例は、日本の兵庫県神戸のフカエ・インダストリアル・カンパニーからのフカエ(Fukae)型高速ミキサー、および日本の大阪府大阪のパワーレックス・カンパニーからのリボン(Ribbon)ミキサーである。

【0049】本明細書中で記載のすべての%および比率は、特に断らない限り、重量基準である。本明細書中で述べるすべての文書は、参考文献として編入する。

【0050】本発明を下記の例によって例示するが、下記の例は、本発明を限定するものではない。

【0051】例I

下記の組成および密度290g/リットルを有する噴霧乾燥界面活性剤粒状物を、下記のように緻密化する。

脂肪アルコールサルフェート	9.0%
直鎖アルキルベンゼンスルホネート	30.0
炭酸ナトリウム	21
ケイ酸ナトリウム	16
硫酸ナトリウム	8
ポリエチレングリコール	0.3
増白剤	0.4
水分	4
他の通常の成分	11.3
計	100%

【0052】噴霧乾燥洗剤粒状物をコンパクターロールの上部に配置されたフォースフィーダーを介してロール型コンパクターユニットの上部上に連続的に装入して、チップを製造する。パイロットコンパクターユニット操作条件は次の通りである：ロールの回転速度は3.60rpmであり、ロールのアンメーターは5.5Aであり、ロール圧力は1.7~2.1トンであり且つフォースフィーダーの回転速度は約16.8rpmであり、フォースフィーダーのアンメーターは3.0Aである。コンパクト化速度はチップとして約56kg/時間である。ロールから出て来るチップ密度は、1.3~1.6g/ccである。チップ中の界面活性剤量は、39%のままである。

【0053】界面活性剤チップをパイロットグラインダー(フィッツ・ミル)に一定に供給する。パイロットグラインダー操作条件は次の通りである：シャフトの回転速度は約4726rpmであり、シャフトのアンメーターは6.0~7.2Aであり且つ打抜きサイズ2.0mmの篩を使用する。粉碎チップの850m上の%は4.0~10.0%である。150m未満の%は19~22%である。粉碎チップの嵩密度は、粉碎したままで約660g/lである。この粉碎粒状物中の界面活性剤量は、約39%のままである。

【0054】緻密化粉碎粒状物9.85kgおよびC₁₆第二級アルキル硫酸ナトリウム(アルキル硫酸ナトリウム95%、硫酸ナトリウム2%、水分/雑多な成分3%)粉末1.58kgをパイロットレディゲKMミキサー(容量50リットル)に装入する。充填量は、完成品の仮の嵩密度700g/lに従って37%である。チョッパー速度を3000rpmに保ちながら、ブレード速度を35rpmに設定する。粉碎界面活性剤粒状物およびアルキルサルフェート粉末をレディゲミキサー中で70秒間よく混合する。次いで、ポリビロリドン(染料移動抑制剤)30gをレディゲミキサー内に25~30秒間噴霧する。次いで、70℃に加熱されたC₁₄~C₁₅EO₉アルキルエトキシレート非イオン界面活性剤440gをレディゲミキサー中で物質上に50~60秒間噴霧する。次いで、ゼオライト13X810g、疎水性沈降シリカ50gおよび防汚重合体100gをレディゲミキサーで2

00秒間添加／混合する。次いで、香料40gをミキサー内に30～40秒間噴霧する。得られた製品の界面活性剤量は、約45％である。この製品を1180mの篩

で篩分ける。篩分けられた製品は、合計界面活性剤量約45％を有する。この製品は、嵩密度781g/lを有する自由流動性粒状物である。

【手続補正書】

【提出日】平成8年11月1日

【手続補正1】

【補正対象書類名】明細書

【補正対象項目名】特許請求の範囲

【補正方法】変更

【補正内容】

【特許請求の範囲】

【請求項1】(a)粒状洗剤組成物と液体バインダー物質との混合物を調製し(ただし、前記粒状洗剤組成物は洗剤界面活性剤を含み且つ前記液体バインダーの量は前記粒状洗剤組成物の約1～約6重量％である)、

(b)工程(a)で調製した組成物とゼオライトXとの混合物を調製する(ただし、ゼオライトXの量は工程(a)で調製した組成物中の液体バインダーの重量に少なくとも等しい)ことを特徴とする、凝集洗剤組成物の製法。

【請求項2】ゼオライトXの量が工程(a)で調製した組成物中の液体バインダーの重量の約1～約2.5倍である、請求項1に記載の方法。

【請求項3】バインダーが有機液体である、請求項2に記載の方法。

【請求項4】バインダーが平均3～16個のアルコキシ基を有するアルコキシ化 $C_{12} \sim C_{18}$ アルコールである、請求項2に記載の方法。

【請求項5】疎水性沈降シリカを前記混合物の約0.1％～約1％である量で工程(b)で調製した混合物に配合する、請求項2に記載の方法。

【請求項6】工程(a)の粒状洗剤が、工程(a)で使用する前にコンパクト化に付してトラップされた空気を除去した噴霧乾燥粒状物である、請求項2に記載の方法。

【請求項7】工程(a)の造粒洗剤組成物が洗剤界面活性剤約20％～約95％および洗浄性ビルダー約5％～約50％を含む、請求項1ないし6のいずれか1項に記載の方法。

【請求項8】洗剤界面活性剤が陰イオン合成界面活性剤である、請求項7に記載の方法。

【請求項9】洗浄性ビルダーがホスフェート、ポリホスフェート、ホスホネート、ポリホスホネート、カーボネート、ボレート、ポリヒドロキシスルホネート、ポリアセテート、カルボキシレート、およびポリカルボキシレートからなる群から選ばれる、請求項8に記載の方法。

【請求項10】(a)粒状洗剤組成物と液体バインダー物質との混合物を調製し(ただし、前記粒状洗剤組成物

は洗剤界面活性剤を含み且つ前記液体バインダーの量は前記粒状洗剤組成物の約1～約6重量％である)、

(b)工程(a)で調製した組成物とゼオライトXとの混合物を調製する(ただし、ゼオライトXの量は工程(a)で調製した組成物中の液体バインダーの重量に少なくとも等しい)方法によって製造されたことを特徴とする、凝集洗剤組成物。

【請求項11】ゼオライトXの量が工程(a)で調製した組成物中の液体バインダーの重量の約1～約2.5倍である、請求項10に記載の製品。

【請求項12】疎水性沈降シリカを前記混合物の約0.1％～約1％である量で工程(b)で調製した混合物に配合する、請求項11に記載の製品。

【請求項13】バインダーが有機液体である、請求項11に記載の製品。

【請求項14】バインダーが平均3～16個のアルコキシ基を有するアルコキシ化 $C_{12} \sim C_{18}$ アルコールである、請求項11に記載の製品。

【請求項15】工程(a)の造粒洗剤組成物が洗剤界面活性剤約20％～約95％および洗浄性ビルダー約5％～約50％を含む、請求項10ないし13のいずれか1項に記載の製品。

【請求項16】洗剤界面活性剤が陰イオン合成界面活性剤である、請求項15に記載の製品。

【請求項17】洗浄性ビルダーがホスフェート、ポリホスフェート、ホスホネート、ポリホスホネート、カーボネート、ボレート、ポリヒドロキシスルホネート、ポリアセテート、カルボキシレート、およびポリカルボキシレートからなる群から選ばれる、請求項16に記載の製品。

【請求項18】バインダーが水溶液である、請求項2に記載の方法。

【請求項19】バインダーが水である、請求項18に記載の方法。

【請求項20】バインダーが水溶液である、請求項11に記載の製品。

【請求項21】バインダーが水である、請求項20に記載の製品。

【手続補正2】

【補正対象書類名】明細書

【補正対象項目名】0046

【補正方法】変更

【補正内容】

【0046】任意の物質

場合によって、洗剤組成物で有用な他の物質が、本法の工程(a)で洗剤成分として配合できる。或いは、このような物質は、ゼオライトX、またはゼオライトXおよび沈降シリカと混合した後に凝集体に添加することができる。任意の物質としては、追加の種類の界面活性剤、例えば、両性界面活性剤、双性界面活性剤および陽イオン界面活性剤が挙げられる。このような界面活性剤の例は、1972年5月23日発行のノリスの米国特許第3,664,961号明細書および1980年10月14日発行のキャンバーの米国特許第4,228,044号明細書(ここに参考文献として編入)に開示されている。他の任意成分としては、漂白剤、増白剤、漂白活性剤、増泡剤、抑泡剤、曇り防止剤および腐食防止剤、汚れ沈殿防止剤、移染防止剤、再付着防止剤、染料移動抑制剤、殺菌剤、pH調整剤、キレート化剤、粘土および酵素が挙げられる。

【手続補正3】

【補正対象書類名】明細書

【補正対象項目名】0048

【補正方法】変更

【補正内容】

【0048】自由流動性緻密化凝集体を製造するために本法を行うのに好ましい方法においては、陰イオン界面活性剤および場合によって追加の乾燥粒状洗剤成分を含む噴霧乾燥粒状製品は、例えば、この粒状組成物を新東工業株式会社からのBCS25型コンパクターなどのコンパクターに通過させることによってコンパクト化に付して空気を除去し、それによってチップを形成する。次いで、これらのチップを粉砕し(例えば、フィッツ・ミル中で)、篩分けして所望の粒径を得ることができる。次いで、緻密化粒子を非イオンバインダーと混合し、ゼオライトX(またはゼオライトXプラス沈降シリカ)と接触させる。好ましくは、液体バインダーを、混合時に(しかし、ゼオライトXを加える前)洗剤組成物上に噴霧することによって粒状洗剤組成物に加える。粒状洗剤(緻密化されているか緻密化されていないかのいずれにせよ)とバインダーとの混合、およびゼオライトXとの接触は、好適なミキサー中で達成することができる。好適なミキサーの例は、日本の兵庫県神戸の深江工業株式会社からのフカエ(Fukae)型高速ミキサー、および日本の大阪府大阪の株式会社パウレックからのリボン(Ribbon)ミキサーである。

【手続補正4】

【補正対象書類名】明細書

【補正対象項目名】0052

【補正方法】変更

【補正内容】

【0052】噴霧乾燥洗剤粒状物をコンパクターロールの上部に配置されたフォースフィーダーを介してロール型コンパクターユニットの上部上に連続的に装入して、

チップを製造する。パイロットコンパクターユニット操作条件は次の通りである: ロールの回転速度は3.60rpmであり、ロールの電流値は5.5Aであり、ロール圧力は1.7~2.1トンであり且つフォースフィーダーの回転速度は約16.8rpmであり、フォースフィーダーの電流値は3.0Aである。コンパクト化速度はチップとして約56kg/時間である。ロールから出て来るチップ密度は、1.3~1.6g/ccである。チップ中の界面活性剤量は、39%のままである。

【手続補正5】

【補正対象書類名】明細書

【補正対象項目名】0053

【補正方法】変更

【補正内容】

【0053】界面活性剤チップをパイロットグラインダー(フィッツ・ミル)に一定に供給する。パイロットグラインダー操作条件は次の通りである: シャフトの回転速度は約4726rpmであり、シャフトの電流値は6.0~7.2Aであり且つ打抜きサイズ2.0mmの篩を使用する。粉砕チップの850m上の%は4.0~10.0%である。150m未満の%は19~22%である。粉砕チップの嵩密度は、粉砕したままで約660g/lである。この粉砕粒状物中の界面活性剤量は、約39%のままである。

【手続補正6】

【補正対象書類名】明細書

【補正対象項目名】0054

【補正方法】変更

【補正内容】

【0054】緻密化粉砕粒状物9.85kgおよびC₁₆。第二級アルキル硫酸ナトリウム(アルキル硫酸ナトリウム95%、硫酸ナトリウム2%、水分/雑多な成分3%)粉末1.58kgをパイロットレディゲKMミキサー(容量50リットル)に装入する。充填量は、完成品の仮の嵩密度700g/lに従って37%である。チョッパー速度を3000rpmに保ちながら、ブレード速度を35rpmに設定する。粉砕界面活性剤粒状物およびアルキルサルフェート粉末をレディゲミキサー中で70秒間よく混合する。次いで、ポリピロリドン(移染防止剤)30gをレディゲミキサー内に25~30秒間噴霧する。次いで、70℃に加熱されたC₁₄~C₁₅EO₉。アルキルエトキシレート非イオン界面活性剤440gをレディゲミキサー中で物質上に50~60秒間噴霧する。次いで、ゼオライト13X810g、疎水性沈降シリカ50gおよび再付着防止剤100gをレディゲミキサーで200秒間添加/混合する。次いで、香料40gをミキサー内に30~40秒間噴霧する。得られた製品の界面活性剤量は、約45%である。この製品を1180mの篩で篩分ける。篩分けられた製品は、合計界面活性剤量約45%を有する。この製品は、嵩密度7

フロントページの続き

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(71) 出願人	592043805			
	ONE PROCTER & GANBL			
	E PLAZA, CINCINNATI,			
	OHIO, UNITED STATES			
	OF AMERICA			

(b) 工部局工程處擬在該處興建一座新渠，以改善該處排水系統，並會與有關方面商討，以確保該處排水系統能正常運作。

【 外国語明細書 】

1 Title of Invention

PROCESS FOR MAKING AGGLOMERATED DETERGENT COMPOSITIONS
HAVING IMPROVED FLOWABILITY

2 Claims

1. A process of forming agglomerated detergent compositions comprising the steps of:
 - (a) forming a mixture of a granular detergent composition and a liquid binder material wherein the granular detergent composition comprises a deterative surfactant, and the amount of said liquid binder is from about 1% to about 6% by weight of said granular detergent composition, and
 - (b) forming a mixture of the composition produced in Step (a) with Zeolite X, wherein the amount of Zeolite X is at least equal to the weight amount of liquid binder in the composition produced in Step (a).
2. The process of Claim 1 wherein the amount of Zeolite X is from about 1 to about 2.5 times the weight amount of liquid binder in the composition produced in Step (a).
3. The process of claim 2 wherein the binder is an organic liquid.
4. The process of claim 2 wherein the binder is an alkoxylated C₁₂ to C₁₈ alcohol having an average of 3 to 16 alkoxy groups.
5. The process of Claim 2 wherein hydrophobic precipitated silica is included in the mixture formed in Step (b) in an amount which is from about 0.1% to about 1% of said mixture.
6. The process of Claim 2 wherein the granular detergent of Step (a) is a spray dried granule which has been subjected to compaction to remove entrapped air prior to use in Step (a).
7. The process of any one of Claims 1 through 6 wherein the granulated detergent composition of Step (a) comprises from about 20% to about 95% deterative surfactant and from about 5% to about 50% detergency builder.

8. The process of Claim 7 wherein the deterative surfactant is an anionic synthetic surfactant.
9. The process of Claim 8 wherein the detergency builder is selected from the group consisting of phosphates, polyphosphates, phosphonates, polyphosphonates carbonates, borates, polyhydroxy sulfonates, polyacetates, carboxylates, and polycarboxylates.
10. An agglomerated detergent composition prepared by the process of;
 - (a) forming a mixture of a granular detergent composition and a liquid binder material wherein the granular detergent composition comprises a deterative surfactant, and the amount of said liquid binder is from about 1% to about 6% by weight of said granular detergent composition, and
 - (b) forming a mixture of the composition produced in Step (a) with Zeolite X, wherein the amount of Zeolite X is at least equal to the weight amount of liquid binder in the composition produced in Step (a).
11. The product of Claim 10 wherein the amount of Zeolite X is from about 1 to about 2.5 times the weight amount of liquid binder in the composition produced in Step (a).
12. The product of Claim 11 wherein hydrophobic precipitated silica is included in the mixture formed in Step (b) in an amount which is from about 0.1% to about 1% of said mixture.
13. The product of Claim 11 wherein the binder is an organic liquid.
14. The product of claim 11 wherein the binder is an alkoxylated C₁₂ to C₁₈ alcohol having an average of from 3 to 16 alkoxy groups.
15. The product of any one of Claims 10 through 13 wherein the granular detergent composition of Step (a) comprises from about 20% to about 95% deterative surfactant and from about 5% to about 50% detergency builder.

16. The product of Claim 15 wherein the deterative surfactant is an anionic synthetic surfactant.

17. The product of Claim 16 wherein the detergency builder is selected from the group consisting of phosphates, polyphosphates, phosphonates, polyphosphonates carbonates, borates, polyhydroxy sulfonates, polyacetates, carboxylates, and polycarboxylates.

3 Detailed Description of Invention

TECHNICAL FIELD

The invention relates to the manufacture of high density, free flowing agglomerated detergent granules, using a liquid binding agent and zeolite X as a flow aid.

BACKGROUND OF THE INVENTION

Recently there has been considerable interest within the detergent industry in the production of detergent granules having relatively high bulk density, e.g. 600 g/liter and above.

Typically, detergent granules, which comprise organic surfactant and inorganic or organic builders are prepared by spray drying an aqueous slurry of the components. The granules thus obtained typically have a density of from about 300 to about 500 g/liter. To meet the requirement for higher density detergent products various processes have been developed for providing such products.

U.S. Pat 5,133,924, Appel et al, issued July 28 1992 discloses a process wherein a spray-dried detergent composition or a mixture of particulate components of a detergent composition is subjected to a two-stage mixing process in order to reduce the porosity of the particles, thereby increasing density. Liquids, such as water or nonionic surfactants are optionally added to the second stage mixer.

U.S. Pat. No. 5,164,108, Appel et al., issued November 17, 1992, discloses a process for making high density detergent powder wherein a liquid acid precursor of an anionic surfactant, a solid, water-soluble alkaline builder and optionally other detergent materials are fed to a high speed mixer/densifier in which the liquid acid precursor is neutralized, thereby producing a powder and then mixing the powder in a moderate speed mixer to reduce the porosity of the powder particles. the patent states that complications can arise with respect to particle size distribution in cases where

high active (i.e., 20% or more surfactant) compositions are processed. It is disclosed that these problems can be obviated by adding a powdered material such as Zeolite A to the second mixer.

Jap. Pat. Application 61-69897, published April 10, 1986 discloses a process for producing a dense agglomerated detergent product from spray dried detergent granules comprising a surfactant and builder, wherein the granules are pulverized by vigorous stirring in a blade mixer, followed by mixing with a binder (e.g., nonionic surfactant) and a "surface improving agent", which can be an aluminosilicate.

U.S. Pat. No. 4,652,391 (Balk), issued March 24, 1987, discloses spray dried detergent granules in which the surfactant is a nonionic. The patent indicates that the granules coming from the spray tower should be cooled rapidly to prevent nonionic from diffusing to the surface of the granules. Such diffusion of nonionic reduces the fluidity and density of the granular product. It is stated that if warm weather prevents rapid cooling, the granules can be "dusted" with a "fluidizing agent" (also referred to as an "anti caking agent"). Synthetic Zeolites (Zeolite A and Zeolite X) are disclosed for this purpose.

BACKGROUND ART

See U.S. Pats. 5,133,924, 5,164,108, 4,656,391 and Japanese Pat. Appln. 61-69897, discussed *supra*, and Perry's Chemical Engineers' Handbook 6th Edition (1984) at Page16-9.

SUMMARY OF THE INVENTION

The present invention is directed to a process of forming agglomerated detergent compositions comprising the steps of;

- (a) forming a homogeneous mixture of a granular detergent composition and a liquid binder material, wherein the granular detergent composition comprises a deterative surfactant, and the amount of said liquid binder material is from about 1% to about 6% by weight of said granular detergent composition, and
- (b) contacting the mixture formed in Step (a) with Zeolite X, wherein the amount of Zeolite X is at least equal to, and preferably from 1 to about 2.5 times, the weight amount of liquid binder in Step (a).

The present invention also encompasses the composition of the above process.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to the preparation of agglomerated detergent granules wherein granular detergent material is mixed with a limited amount of a liquid binder material, thereby resulting in agglomerates having an increased particle size compared to the original detergent granules.. Experience has shown that agglomerates formed in this manner often tend to be sticky, and therefore have poor free-flow properties. In accordance with the present invention it has been found that for detergent agglomerates which utilize liquid binders, Zeolite X is a particularly effective free-flow aid when applied as a surface coating to said agglomerates. Although Zeolite A is also effective as a free-flow aid and has generally been preferred over Zeolite X for most detergent uses because of its better sequestering power, it has now been found that Zeolite X is a more effective free-flow aid than Zeolite A for detergent agglomerates utilizing liquid binders. Additionally it has been found that the use of Zeolite X as free-flow aid in said agglomerates results in a higher density product than obtained when using Zeolite A. Typically, the products produced by the process herein have a bulk density of greater than 600 grams/liter.

Granular Detergent Compositions

The granular detergent composition in Step (a) of the process of the present invention comprises a deterative surfactant. The surfactant and any other components of the granular compositions can be introduced into Step (a) as separate ingredients or as a pre-formed composition, such as a spray dried detergent composition or as a mixture of one or more separate granular ingredients and a spray dried detergent composition.

Anionic surfactants are the preferred surfactants for use herein and are well known in the art. The following are representative examples of such surfactants.

Anionic surfactants suitable for use herein include the water-soluble salts, preferably the alkali metal, ammonium and alkylammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher (C₈-18 carbon atoms) primary or secondary alcohols such as those produced by reducing the glycerides of

tallow or coconut oil or by the oxo process; and the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patents 2,220,099 and 2,477,383, incorporated herein by reference. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13.

Other anionic surfactants suitable for use herein are the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium or potassium salts of sulfuric acid esters of the reaction product of one mole of a fatty alcohol (e.g. coconut or tallow alcohol) with 1 to 6 moles of ethylene oxide; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates having about 1 to 10 units of ethylene oxide per molecule and in which the alkyl radicals contain about 8 to 12 carbon atoms.

In addition, suitable anionic surfactants include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxyalkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin and paraffin sulfonates containing from about 12 to 20 carbon atoms; and beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Preferred anionic surfactants are the alkali metal salts of C₁₀₋₁₈ linear alkylbenzene sulfonate and C₁₀₋₁₈ alkyl sulfate. A preferred embodiment of the present invention is wherein the anionic surfactant comprises from about 20% to about 40% of a mixture of sodium C₁₀₋₁₃ linear alkylbenzene sulfonate and sodium C₁₂₋₁₆ alkyl sulfate in a weight ratio of about 2:1 to 1:2.

Water-soluble salts of the higher fatty acids, i.e., "soaps", are also useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkylammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils

or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

Other types of surfactants suitable for use in the granular detergent compositions of step (a) includes nonionic, cationic ampholytic, and zwitterionic types.

Typical nonionic surfactants include the alkylene oxide condensates of hydrocarbyl groups (e.g. alkyl or alkyl phenyl) wherein the hydrocarbyl groups contain from about 8 to about 22 carbon atoms. Nonionics also include semi polar compounds such as C₈-C₂₂ amine oxides. An extensive discussion of nonionic surfactants is found in U.S. Pat. 5,338,491 Conner, et al issued August 16, 1994. Nonionics also include fatty acid amide surfactants of the formula



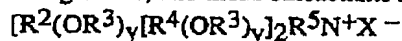
wherein: R₁ is H, C₁-C₈ hydrocarbyl, 2-hydroxyethyl, 2-hydroxypropyl, or a mixture thereof, preferably C₁-C₄ alkyl, more preferably C₁ or C₂ alkyl, most preferably C₁ alkyl (i.e., methyl); and R₂ is a C₅-C₃₂ hydrocarbyl moiety, preferably straight chain C₇-C₁₉ alkyl or alkenyl, more preferably straight chain C₉-C₁₇ alkyl or alkenyl, most preferably straight chain C₁₁-C₁₉ alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 2 (in the case of glyceraldehyde) or at least 3 hydroxyls (in the case of other reducing sugars) directly connected to the chain, or an alkoxyated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose, as well as glyceraldehyde. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of -CH₂-(CHOH)_n-CH₂-OH, -CH(-CH₂-OH)-(CHOH)_n-1-CH₂-OH, -CH₂-(CHOH)₂(CHOR')(CHOH)-CH₂-OH, where n is an integer from 1

to 5, inclusive, and R' is H or a cyclic mono- or poly- saccharide, and alkoxyated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly -CH₂-(CHOH)₄-CH₂-OH.

In the above formulas, R₁ can be, for example, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, 2-hydroxy ethyl, or 2-hydroxy propyl. For highest sudsing, R₁ is preferably methyl or hydroxyalkyl. If low sudsing is desired, R₁ is preferably C₂-C₈ alkyl, especially n-propyl, iso-propyl, n-propyl, iso-propyl, n-butyl, iso-butyl, pentyl, hexyl and 2-ethyl hexyl.

Specific examples of this type of amide surfactant include C₁₂-N-(3-methoxypropyl) glucamide and coconut n-methyl glucamide. Further disclosure of this type of amide surfactant can be found in U.S. Pat. 5,376,310, Cripe, issued December 27, 1994.

Cationic deterative surfactants include the ammonium surfactants such as alkyldimethylammonium halogenides, and those surfactants having the formula:



wherein R² is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R³ is selected from the group consisting of -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂-, and mixtures thereof; each R⁴ is selected from the group consisting of C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, benzyl, ring structures formed by joining the two R⁴ groups, CH₂CHOHCHOHCOR₆CHOHCH₂OH wherein R₆ is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R⁵ is the same as R⁴ or is an alkyl chain wherein the total number of carbon atoms of R² plus R⁵ is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Other cationic surfactants useful herein are also described in U.S. Pat. No. 4,228,044, Cambre, issued Oct. 14, 1980. Ampholytic surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate. See U.S. Pat. No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35 for examples of ampholytic surfactants. Zwitterionic

surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Pat. No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48 for examples of zwitterionic surfactants.

A further extensive disclosure of various types of surfactants can be found in US Pat. 3,664,961, Norris, issued May 23, 1972.

Surfactant will generally comprise from about 20% to about 95%, preferably from about 30% to about 60%, of the granular detergent composition of Step (a) prepared by the process herein.

Typically detergent compositions made by the present process will contain builders. Builders useful in the present invention are generally selected from the various water-soluble, alkali metal, ammonium or substituted ammonium phosphates, polyphosphates, phosphonates, polyphosphonates, carbonates, borates, polyhydroxy sulfonates, polyacetates, carboxylates, and polycarboxylates. Preferred are the alkali metal, especially sodium, salts of the above. Preferred for use herein are the phosphates, carbonates, silicates, polycarboxylates, and mixtures thereof. More preferred are sodium tripolyphosphate, tetrasodium pyrophosphate, sodium citrate, sodium tartrate sodium mono- and di-succinates, and mixtures thereof.

Specific examples of inorganic phosphate builders are sodium and potassium tripolyphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from about 6 to 21, and orthophosphates. Other phosphorus builder compounds are disclosed in U.S. Patents 3,159,581; 3,213,030; 3,422,137; 3,400,176 and 3,400,148, all of which are incorporated herein by reference.

Examples of nonphosphorus, inorganic builders are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and Zeolites such as Zeolite A. Water-soluble, nonphosphorus organic builders useful herein include the various alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxy sulfonates. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid.

Polymeric polycarboxylate builders are set forth in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. Such materials include the water-soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalononic acid.

Other suitable polycarboxylates for use herein are the polyacetal carboxylates described in U.S. Patent 4,144,226, issued March 13, 1979 to Crutchfield et al., and U.S. Patent 4,246,495, issued March 27, 1979 to Crutchfield et al.

Builders generally comprise from about 5% to about 50%, preferably from about 20% to about 40% of compositions prepared by the process herein. Builders can be included in the granular detergent composition of Step (a) or they can be added to the agglomerates after they have been mixed with the Zeolite X.

Filler materials such as sodium sulfate or sodium chloride are typically present in the detergent compositions of Step (a) at levels up to about 40%.

Binder

A wide variety of liquids can be used as the binder for the granular detergent components in Step (a) of the process of the invention.

Water is a suitable binder. Likewise aqueous solutions containing up to about 65%, preferably up to about 55%, more preferably up to about 35% of inorganic or organic materials such as sodium silicate (2.0 ratio $\text{Na}_2\text{O}:\text{SiO}_2$) or polyacrylate polymer can be used. Generally solute levels above about 65% result in aqueous dispersions or solutions which are too viscous to be conveniently worked into a homogeneous mixture with the granular detergent of Step (a) of the process herein. Also, the preferred way of introducing the liquid binder into the process is by spraying it onto the granular detergent. Highly viscous solutions are difficult to spray.

Nonionic organic liquids (melting point below about 7 degrees C) are preferred binders for use in the process of the invention. Preferred materials are the nonionic surfactants since they will contribute to the cleaning performance of the compositions. See the discussion of nonionic surfactants *supra*. The most common types of these materials are alkoxyated long chain organic compounds.

Alkoxyated nonionic materials suitable for use as binders herein include condensation products of C₁₂₋₁₈ fatty alcohols with an average of 3 to 20, preferably 4 to 16, alkoxy moieties. The alcohol radicals may be saturated or monounsaturated, linear or methyl-branched in the 2-position (oxo radical), and may be derived from naturally occurring or hydrogenated fatty residues and/or synthetic residues. Ethoxylates derived from cetyl, stearyl and oleyl alcohol and mixtures thereof are particularly suitable. Examples are tallow fatty alcohols containing on average from 4 to 8 ethylene oxide (EO) moieties, tallow fatty alcohol containing on average from 10 to 18 EO and oleyl alcohol containing on average from 6 to 12 EO and also mixtures thereof.

Other nonionic materials are alkoxyated C₁₂₋₂₄, preferably C₁₄₋₁₈ alcohols in the production of which 1 to 3 mols of propylene oxide and then 4 to 20, preferably 4 to 7, mols of ethylene oxide are added onto the alcohol. Ethoxylated C₈₋₁₂-alkyl-phenols containing 4 to 14 EO are also suitable.

Nonionic organic liquids which are not surfactants can also be used as binders herein. Examples of such materials are polyethylene glycols and polypropylene glycols.

Binders are used in an amount of from about 1% to about 6%, preferably from about 2.5% to about 6%, most preferably from about 3% to about 4.5%, based on the total weight of detergent components in Step (a) of the process.

Zeolite X

In Step (b) of the process herein the agglomerated particles which have been formed from the essential detergent components and binder in Step (a) are contacted and intimately mixed with Zeolite X in an amount which is at least equal to the amount of liquid binder used in Step (a) of the process. Preferably the amount of Zeolite X is from 1 to 2.5 times the weight amount of liquid binder used in Step (a).

Zeolite X is a synthetic aluminosilicate, readily available commercially from, for example, Union Carbide Company and Philadelphia Quartz Company. The sodium salt form (Zeolite 13X) has a pore size of about 8 Angstroms and the calcium form (Zeolite 10X) a pore size of about 7 Angstroms. For use herein, the sodium form is preferred. The Zeolite X should be in powdered form having particle size of less than about 20 millimicrons. Preferred particle sizes are in the range of from about 5 to about 10 millimicrons.

It has been found that further improvement in the free flow properties and increased density of compositions made by the process herein can be achieved if hydrophobic precipitated silica is included along with Zeolite X in Step (b) of the process.

Hydrophobic precipitated silicas suitable for use herein are commercially available, for example Supernat D 10 and D 17 from Degussa AG, Frankfurt/Main, Germany.

When used in Step (b) of the process, the amount of hydrophobic precipitated silica is from about 0.1% to about 1%, preferably from about 0.2% to about 0.4%, based on the weight of the mixture in Step (a).

Optional Materials

Optionally, other materials useful in detergent compositions can be included as detergent components in Step (a) of the process herein. Alternatively, such materials can be added to the agglomerates after they have been mixed with Zeolite X, or Zeolite X and precipitated silica. Optional materials include additional types of surfactants such as ampholytics, zwitterionics and cationics. Examples of such surfactants are disclosed in U.S. Patents 3,664,961, Norris, issued May 23, 1972, and 4,228,044, Cambro, issued October 14, 1980, incorporated by reference herein. Other optional ingredients include bleaches, brighteners, bleach activators, suds boosters, suds suppressors, anti-tarnish and anti-corrosion agents, soil suspending agents, dye transfer inhibition agents, soil release agents, dye transfer inhibiting agents, germicides, pH adjusting agents, chelating agents, clays and enzymes.

Processing

A particulate composition comprising surfactant is used in Step (a) of the process. This composition can consist of granules from a spray drying tower or one or more particulate materials which have not been spray dried. Alternatively, the composition can be a mixture of spray dried granules and other particulate detergent components such as additional surfactant and/or builder, bleach, etc..

Prior to mixing with binder, the particulate composition can be densified. For example it can be subjected to mixing in a high speed mixer such as a Loedige CB, Shugi Granulator, or Drais K-TTP, followed by mixing in a moderate speed mixer

such as the Loedige KM or Drais K-T. See for example; U.S. Pats. 5,133,924 and 5,164,108. The mixing of densified detergent particles and binder and the contacting of said mixture with Zeolite X (or Zeolite X plus precipitated silica) is accomplished in the moderate speed mixer.

In a preferred way of carrying out the process to produce free flowing, densified agglomerates, a spray dried granular product comprising anionic surfactant and, optionally, additional dry particulate detergent components is subjected to compaction to remove air, for example by passing the particulate composition through a compactor such as the BCS25 type compactor from Shinto Industrial Company, thereby forming chips. These chips then can be ground (e.g. in a Fitz Mill), and screened to produce the desired particle size. The densified particles are then mixed with nonionic binder and contacted with Zeolite X (or Zeolite X plus precipitated silica). Preferably, the liquid binder is added to the granular detergent composition by spraying it onto the detergent composition during the mixing, but prior to adding Zeolite X. The mixing of particulate detergent (whether densified or not) with binder, and the contact with Zeolite X can be accomplished in any suitable mixer. Examples of suitable mixers are the Fukae Vertical High Speed Mixer from Fukae Industrial Company, Hogo prefecture, Kobe Japan, and the Ribbon Mixer from Powerex Company, Osaka prefecture, Osaka Japan

All percentages and ratios described herein are by weight unless otherwise stated. All documents mentioned herein are incorporated by reference.

The invention will be illustrated by the following example, which is not to be construed in any manner as a limitation of the invention.

EXAMPLE I

A spray dried surfactant granule having the following composition and a density of 290 grams/liter is densified as described below.

Fatty Alcohol Sulfate	9.0%
Linear Alkylbenzene Sulfonate	30.0
Sodium Carbonate	21
Sodium Silicate	16
Sodium Sulfate	8
Polyethylene Glycol	0.3
Brighteners	0.4
Moisture	4
Other conventional ingredients	11.3
<hr/>	
TOTAL	100%

The spray dried detergent granule is continuously loaded onto the top of a roll-type compactor unit via a force feeder that is located at the top of the compactor rolls, to produce chips. Pilot compactor unit operation condition is: the rotation rate of rolls is 3.60 rpm, ammeter of roll is 5.5 A, roll pressure is 1.7-2.1 tons and rotation rate of force feeder is ~16.8 rpm, ammeter of force feeder is 3.0A. Compaction rate is ~56 kgs/hr as chips. Chip density that comes out rolls, is 1.3~1.6 g/cc. The surfactant level in the chips remains at 39%.

The surfactant chips are constantly fed into a pilot grinder (Fitz mill). Pilot grinder operation condition is: the rotation rate of shaft is ~4726rpm, ammeter of shaft is 6.0~7.2 A and 2.0 mm punch out size of screen is used. % on 850 m of the ground chips is 4.0~10.0%. % under 150 m is 19~22%. The bulk density of the ground chips is ~660 g/L as ground. The surfactant level in this ground granule remains~39%.

9.85 kgs of the densified ground granules and 1.58 kgs of sodium C₁₆ secondary alkyl sulfate (95% sodium alkyl sulfate, 2% sodium sulfate, 3% moisture and misc.) powder are loaded into a pilot Lödige KM mixer (50 liter capacity). Fill level is 37% in accordance with the assumed the bulk density of finished product of 700 g/L. The blade speed is set at 35 rpm while keeping chopper speed at 3000 rpm. The ground surfactant granule and alkyl sulfate powder are well mixed in the Lödige mixer during 70 sec. 30 g of polypyrrolidone (dye transfer inhibition agent) is then sprayed into Lödige mixer during 25-30 sec. 440 g of C₁₄-C₁₅ EO₉ alkyl ethoxylate nonionic which has been heated to 70°C is then sprayed onto the material in the Lödige mixer during a time period of 50 to 60 seconds. Then 810g of Zeolite 13X, 50 g of hydrophobic precipitated silica and 100 g of soil release polymers are added/mixed into Lödige mixer during 200 sec. Then, 40 g of perfume is sprayed into mixer during 30-40 sec. The surfactant level of the resulting product is ~45%. The product is sieved through an 1180 m screen. The sieved product has a total surfactant level of ~45%. The product is a free flowing granule having a bulk density of 781 g/L.

1 Abstract

Zeolite X is used in the process for manufacture of detergent agglomerates to improve flowability of the finished product.

2 Representative Drawing

None

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